[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

Solubility Studies. VII. The Solubilities of Some Isomeric Ketones in Water

By John H. Saylor, Victor J. Baxt[1] and Paul M. Gross

The possible existence of a linear relationship between the heats and entropies of solution of organic compounds has been suggested by several investigators[2,3] and is of considerable interest from the standpoint of the energy relationships involved in the solution process.

In a previous communication from this Laboratory[4] it was shown that a linear relationship between the heats and entropies of solution existed for three of the ketones studied. These ketones, methyl propyl, methyl isopropyl and diethyl, have approximately the same molar volumes at the temperatures of the measurements. It was suggested that equality of solute volumes as well as chemical similarity may well be a prerequisite for the existence of such a linear relationship between the heats and entropies of solution. The present investigation of the solubilities of the three isomeric ketones, dipropyl, diisopropyl and methyl n-amyl, was undertaken with this suggestion in mind.

Experimental

The saturated solutions were prepared and analyzed by means of a Zeiss combination liquid and gas interferometer as previously described.[4,5]

The ketones were obtained from the Carbide and Carbon Chemical Company. They were purified by repeated shaking with ammoniacal silver nitrate until no discoloration appeared on allowing the ketone to stand for thirty minutes in contact with fresh reagent. Then they were washed, dried over calcium sulfate and fractionated in a 50-cm. Widmer still using calibrated thermometers. The boiling points of the fractions used are given in Table I.

It was necessary to determine the densities of diisopropyl and methyl n-amyl ketone in order to calculate the corresponding molar volumes. This was done at 10, 30, 50 and 75° by means of appropriate specific gravity bottles.

Results

The observed solubilities are listed in Table II. Vapor solubilities,[4,10] C_s, were calculated from these and are listed in Table II along with the vapor pressures, P_L, of the solute. The vapor solubility is defined as that concentration C_s in equilibrium with the vapor of the substance under a standard pressure of 100 mm. at the particular temperature in question. It is calculated by means of Henry's law from the observed solubilities and the vapor pressure of the liquid solute at the same temperature.

Table II also lists the mole fraction, N, corresponding to C_s as well as the densities and molar volumes, V_m, at each temperature.

The free energies of hydration as given by the relation $\Delta F = RT \ln (P/N)$ have been calculated from the mole fractions, N, given in Table II. The corresponding entropy of hydration ΔS was evaluated graphically from a plot of ΔF vs. T. The heats of hydration ΔH were calculated from the values of ΔF and ΔS by means of the relation

$$\Delta F = \Delta H - T\Delta S$$

These quantities are listed in Table III.

Figure 1 is a plot of ΔS versus ΔH for dipropyl, diisopropyl and methyl n-amyl ketones as well as for methyl propyl, methyl isopropyl and diethyl ketones taken from the previous investigation. The linear relationship is not as good in the present investigation. Nevertheless, within the limits of experimental error and the assumptions involved the data point to its validity. It is likely that the relation may have limited validity for the longer carbon chains with their many possible configurations. Butler[3] has shown that such a linearity exists in a series of alcohols. It

TABLE I

BOILING POINTS OF THE COMPOUNDS

Substance	B. p. at 760 mm., °C.	Previously observed b. p., °C.	Ref.
Dipropyl ketone	144.00–144.10	144.1	6
Diisopropyl ketone	124.06 ± 0.05	124.0 123.7	7, 8
Methyl n-amyl ketone	150.18–150.32	150.2	9

(1) This paper was taken in part from the thesis submitted by Victor J. Baxt to the Graduate School of Duke University in partial fulfillment of the requirements for the degree of Master of Arts, June, 1940.

(2) Evans and Polanyi, *Trans. Faraaay Soc.*, **32**, 1333 (1936).

(3) Butler, *ibid.*, **33**, 229 (1937).

(4) Gross, Rintelen and Saylor, *J. Phys. Chem.*, **43**, 197 (1939).

(5) Gross and Saylor, THIS JOURNAL, **53**, 1747 (1931).

(6) Timmermans, *Bull. soc. chim. belg.*, **30**, 62 (1931).

(7) Mailhe, *Bull. soc. chim.*, [4] **5**, 620 (1909).

(8) "International Critical Tables."

(9) Park and Hoffman, *Ind. Eng. Chem.*, **24**, 132 (1932).

(10) Saylor, Stuckey and Gross, THIS JOURNAL, **60**, 373 (1938).

TABLE II

SOLUBILITIES AND RELATED QUANTITIES

Ketone	t, °C.	Moles per 1000 g. H_2O	C_s molality	$N \times 10^3$	d^t_4	P_L, (mm.)	V_m, (ml.)
Dipropyl[a]	0	0.0643	4.02	69.1	0.8340[11]	1.6[12]	136.9
	10	.0466	1.55	27.2	.8248	3.0	138.4
	30	.0331	0.348	6.23	.8081	9.5	141.3
	50	.0288	.113	2.03	.7913	25.5	144.3
	75	.0254	.336	0.604	.7702	75.6	148.2
Diisopropyl	10	.0587	.858	15.2	.8139	6.8[13]	140.3
	30	.0404	.201	3.60	.7968	20.1	143.3
	40	.0392	.118	2.12	.7869	33.2	145.1
	50	.0350	.0668	1.20	.7792	52.4	146.5
	55	.0339	.0562	1.01	.7734	65.5	147.6
	65	.0331	.0335	0.603	.7645	98.8	149.3
	75	.0376	.0255	.459	.7560	147.3	151.0
Methyl n-amyl	10	.0472	3.35	56.8	.8245	1.41[14]	138.5
	30	.0355	.668	11.9	.8072	5.32	141.4
	50	.0319	.216	3.86	.7898	14.8	144.6
	60	.0308	.110	1.97	.7809	28.0	146.2
	65	.0315	.0890	1.60	.7761	35.4	147.1
	75	.0339	.0610	1.10	.7676	55.6	148.7

[a] Data at 0 and 10° from the data of Gross, Rintelen and Saylor, ref. 4.

TABLE III

VALUES OF ΔF, ΔH AND ΔS

Ketone	t, °C.	ΔF, kcal.	$-\Delta S$, cal./degree	$-\Delta H$, kcal.
Dipropyl	0	3.95	65.8	14.01
	10	4.62	64.5	13.63
	30	5.84	58.1	11.76
	50	6.93	54.1	10.54
	75	8.31	53.0	10.13
Diisopropyl	10	4.94	62.1	12.63
	30	6.16	58.1	11.44
	40	6.70	58.1	11.49
	50	7.27	55.1	10.47
	55	7.50	52.5	9.68
	65	8.07	46.6	7.68
	75	8.50	41.0	5.81
Methyl n-amyl	10	4.20	60.2	12.84
	30	5.44	59.7	12.65
	50	6.52	56.7	11.79
	60	7.17	53.3	10.58
	65	7.42	52.7	10.39
	75	7.90	50.2	9.57

appears, however, that the alcohols with the longest carbon chains do not follow the relationship as closely.

Figure 2 is a plot of vapor solubility against molar volume. There is a still greater temperature dependency in the solubility of these compounds than that found previously for ketones of lower molecular weight. At 10° methyl n-amyl

(11) F. K. Beilstein, "Handbuch der organischen Chemie," 4th ed., Julius Springer, Berlin, Vol. 1, p. 700, appendix 1, Vol. I, p. 359.

(12) Rintelen, Saylor and Gross, THIS JOURNAL, 59, 1129 (1937).

(13) Aston and Mayberry, ibid., 56, 2682 (1934).

(14) Stuckey and Saylor, ibid., 62, 2922 (1940).

ketone is 3.9 times more soluble than diisopropyl ketone but this ratio diminishes with increase in temperature until at 75° it is 2.4. This greater temperature dependency would be predicted from the explanation previously offered.
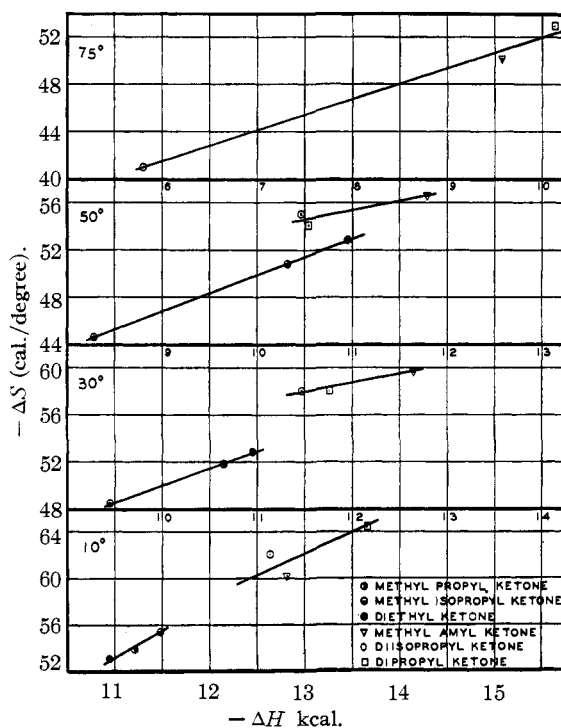

Fig. 1.—Relation between heats and entropies of solution.

According to this, compounds such as methyl n-amyl ketone with longer unbranched side-chains
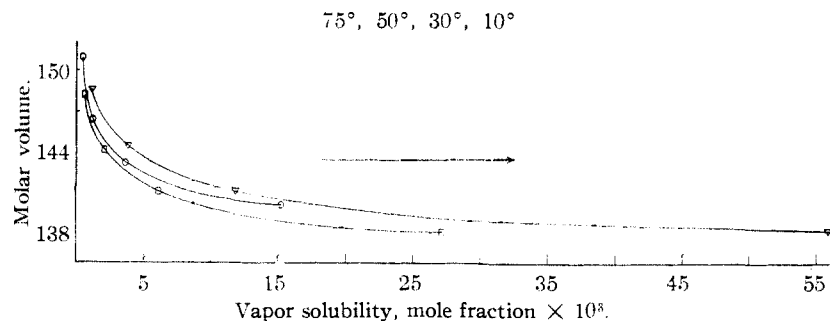
75°, 50°, 30°, 10°

Fig. 2.—Effect of temperature on solubilities in relation to volume: ▽, methyl amyl ketone; O, diisopropyl ketone; ▢, dipropyl ketone.

may be stretched out at low temperatures so that the CH_2 groups are surrounded by the maximum possible number of water molecules, the attractive forces between these groups and water thus adding to the main interaction between the carbonyl dipole and water. When the temperature increases, the molecule may assume other more compact configurations which will be such as to decrease the number of water molecules adjacent to the CH_2 groups. On the other hand, molecules such as that of diisopropyl ketone having compact branched structures can only assume a lim-

ited number of configurations and, hence, their solubilities are less temperature dependent.

Summary

The solubilities in water of dipropyl, diisopropyl and methyl n-amyl ketones have been determined at various temperatures from 10 to 75° and vapor solubilities have been computed.

Free energies, heats and entropies of solution have been calculated. Additional evidence was obtained which tends to confirm the previous suggestion that equality of solute volume as well as chemical similarity is necessary for a linear relation to exist between entropies and heats of solution.

Large solubility differences and a large temperature dependence of these differences were noted in agreement with those previously found for other isomeric ketones.

[CONTRIBUTION FROM THE MALLINCKRODT CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Surface Tension of Solutions of Electrolytes as a Function of the Concentration. IV. Magnesium Sulfate

BY GRINNELL JONES AND WENDELL A. RAY

This paper is a continuation of work previously reported[1] on the surface tensions of aqueous solution of electrolytes relative to that of pure water. These earlier papers should be consulted for a description of the experimental technique and a discussion of the historical and theoretical background of the problem. The data given are "apparent relative surface tensions" in the sense defined in the second paper of this series.

Magnesium sulfate was chosen for this work because none of the salts already studied belonged to this valence type. The measurements have been carried out at 25.00° over a concentration range of 0.0001 up to 2 molar.

Analytical reagent grade magnesium sulfate was purified by two recrystallizations from water. The crystals were washed by centrifugation and

(1) Grinnell Jones and Wendell A. Ray, THIS JOURNAL, **59**, 187 (1937); **63**, 288, 3262 (1941); Grinnell Jones and L. D. Frizzell. J. Chem. Phys., **8**, 986 (1940).

slowly dried in an electric oven. As the salt was hygroscopic each sample before final weighing was kept in an electric furnace at 475° for several hours or until constant weight was assured. At this temperature the anhydrous salt was formed. The samples were weighed in platinum boats in stoppered weighing bottles. A saturated solution showed no red coloration with phenolphthalein. Two 50-ml. Ostwald type pycnometers were used for the density measurements and gave duplicate results differing by not more than a few parts per million. The surface tension measurements were made by the differential capillary rise method as described in the first and second papers of this series. The figures given in Table I are the mean of at least two independent determinations for each concentration. The results are shown graphically in Figs 1 and 2.